

PCT

INTERNATIONAL SEARCH REPORT

(PCT Article 18 and Rules 43 and 44)

Applicant's or agent's file reference PPD 50391/W0	FOR FURTHER ACTION see Notification of Transmittal of International Search Report (Form PCT/ISA/220) as well as, where applicable, Item 5 below.	
International application No. PCT/GB 00/01062	International filing date (day/month/year) 21/03/2000	(Earliest) Priority Date (day/month/year) 01/04/1999
Applicant ZENECA LIMITED et al.		

This International Search Report has been prepared by this International Searching Authority and is transmitted to the applicant according to Article 18. A copy is being transmitted to the International Bureau.

This International Search Report consists of a total of 3 sheets.

☒ It is also accompanied by a copy of each prior art document cited in this report.

1. Basis of the report

- a. With regard to the language, the international search was carried out on the basis of the international application in the language in which it was filed, unless otherwise indicated under this item.

☐ the international search was carried out on the basis of a translation of the international application furnished to this Authority (Rule 23.1(b)).

- b. With regard to any nucleotide and/or amino acid sequence disclosed in the international application, the international search was carried out on the basis of the sequence listing:

☐ contained in the international application in written form.

☐ filed together with the international application in computer readable form.

☐ furnished subsequently to this Authority in written form.

☐ furnished subsequently to this Authority in computer readable form.

☐ the statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.

☐ the statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished.

2. ☐ Certain claims were found unsearchable (See Box I).

3. ☐ Unity of invention is lacking (see Box II).

4. With regard to the title,

☒ the text is approved as submitted by the applicant.

☐ the text has been established by this Authority to read as follows:

5. With regard to the abstract,

☒ the text is approved as submitted by the applicant.

☐ the text has been established, according to Rule 38.2(b), by this Authority as it appears in Box III. The applicant may, within one month from the date of mailing of this international search report, submit comments to this Authority.

6. The figure of the drawings to be published with the abstract is Figure No.

☐ as suggested by the applicant.

☐ because the applicant failed to suggest a figure.

☐ because this figure better characterizes the invention.

☐ None of the figures.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/GB 00/01062

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 A01N25/30 A01N57/20

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 A01N

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 375 624 A (SANDOZ AG) 27 June 1990 (1990-06-27) page 2, line 1 -page 3, line 8 compositions IVa, IVb, IVc, IVd example 3 ---	1-3, 6, 11, 14-17
X	W0 96 32839 A (MONSANTO COMPANY) 24 October 1996 (1996-10-24) page 6, line 7 - line 28 page 14, line 23 - line 30 ---	1-3, 11-17
X	W0 97 32476 A (KAO CORPORATION) 12 September 1997 (1997-09-12) page 2, line 23 -page 5, line 18 page 10, line 17 -page 11, line 16 page 17, line 14 -page 18, line 5 --- -/--	1-3, 11-17



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

22 May 2000

Date of mailing of the international search report

07/06/2000

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Fort, M

INTERNATIONAL SEARCH REPORT

International Application No.

PCT/GB 00/01062

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 668 085 A (JAMES CARNEGIE FORBES) 16 September 1997 (1997-09-16) the whole document	1-3, 11, 14-17
X	WYRILL J B ET AL: "GLYPHOSATE TOXICITY TO COMMON MILKWEED AND HEMP DOGBANE AS INFLUENCED BY SURFACTANTS" WEED SCIENCE, US, WEED SCIENCE SOCIETY OF AMERICA, CHAMPAIGN, IL, vol. 25, no. 3, 1 May 1977 (1977-05-01), pages 275-287, XP002034447 ISSN: 0043-1745 page 277 -page 278	1-3, 11, 14-17

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/GB 00/01062

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
EP 375624	A	27-06-1990	US 5035738 A AT 118671 T AU 629278 B AU 4717189 A BR 8906695 A CA 2006114 A CN 1043601 A,B DE 68921317 D DK 656989 A EG 19012 A ES 2070927 T GR 3015295 T HU 52685 A,B JP 2221204 A JP 2828291 B NZ 231966 A PT 92673 A,B RU 2093505 C TR 24048 A ZA 8909864 A	30-07-1991 15-03-1995 01-10-1992 28-06-1990 11-09-1990 23-06-1990 11-07-1990 30-03-1995 24-06-1990 30-06-1994 16-06-1995 30-06-1995 28-08-1990 04-09-1990 25-11-1998 25-11-1992 08-01-1991 20-10-1997 01-03-1991 28-08-1991
WO 9632839	A	24-10-1996	US 5750468 A AT 187602 T AU 691425 B AU 5325196 A BR 9608102 A CA 2214376 A CZ 9703327 A DE 69605660 D EP 0820231 A ES 2142055 T HU 9801372 A JP 3015107 B JP 10513478 T NZ 305278 A PL 322682 A ZA 9602816 A	12-05-1998 15-01-2000 14-05-1998 07-11-1996 20-07-1999 24-10-1996 18-02-1998 20-01-2000 28-01-1998 01-04-2000 28-09-1998 06-03-2000 22-12-1998 25-02-1999 16-02-1998 02-10-1996
WO 9732476	A	12-09-1997	AU 713956 B AU 2231597 A BR 9702106 A CN 1190327 A EP 0824315 A JP 9295901 A NZ 328990 A US 5948421 A	16-12-1999 22-09-1997 12-01-1999 12-08-1998 25-02-1998 18-11-1997 29-06-1999 07-09-1999
US 5668085	A	16-09-1997	NONE	

PATENT COOPERATION TREATY

PCT

NOTIFICATION OF THE RECORDING OF A CHANGE

(PCT Rule 92bis.1 and
Administrative Instructions, Section 422)

From the INTERNATIONAL BUREAU

To:

RICKS, Michael, James
Syngenta Limited
Intellectual Property Dept.
P.O. Box 3538
Jealott's Hill Research Station
Bracknell RG42 6YA
ROYAUME-UNI

Date of mailing (day/month/year) 16 July 2001 (16.07.01)	Applicant's or agent's file reference PPD 50391/WO
International application No. PCT/GB00/01062	International filing date (day/month/year) 21 March 2000 (21.03.00)

1. The following indications appeared on record concerning:

☒ the applicant
 ☐ the inventor
 ☐ the agent
 ☐ the common representative

Name and Address

SYNGENTA LIMITED
Fernhurst
Haslemere
Surrey GU27 3JE
United Kingdom

State of Nationality

GB

State of Residence

GB

Telephone No.

Facsimile No.

Teleprinter No.

2. The International Bureau hereby notifies the applicant that the following change has been recorded concerning:

☐ the person
 ☐ the name
 ☒ the address
 ☐ the nationality
 ☐ the residence

Name and Address

SYNGENTA LIMITED
Fernhurst
Haslemere
Surrey GU27 3JE
United Kingdom

State of Nationality

GB

State of Residence

GB

Telephone No.

Facsimile No.

Teleprinter No.

3. Further observations, if necessary:

4. A copy of this notification has been sent to:

☒ the receiving Office
 ☐ the designated Offices concerned
☐ the International Searching Authority
 ☒ the elected Offices concerned
☐ the International Preliminary Examining Authority
 ☐ other:

The International Bureau of WIPO 34, chemin des Colombettes 1211 Geneva 20, Switzerland Facsimile No.: (41-22) 740.14.35	Authorized officer <div style="text-align: right;">Dominique DELMAS</div> Telephone No.: (41-22) 338.83.38
---	--

PATENT COOPERATION TREATY

PCT

NOTIFICATION OF THE RECORDING OF A CHANGE

(PCT Rule 92bis.1 and
Administrative Instructions, Section 422)

From the INTERNATIONAL BUREAU

To:

RICKS, Michael, James
Syngenta Limited
Intellectual Property Dept.
P.O. Box 3538
Jealott's Hill Research Station
Bracknell, RG42 6YA
ROYAUME-UNI

Date of mailing (day/month/year) 25 April 2001 (25.04.01)	Applicant's or agent's file reference PPD 50391/WO
International application No. PCT/GB00/01062	IMPORTANT NOTIFICATION
International filing date (day/month/year) 21 March 2000 (21.03.00)	International application No. PCT/GB00/01062

1. The following indications appeared on record concerning:

☒ the applicant
 ☐ the inventor
 ☐ the agent
 ☐ the common representative

Name and Address

ZENECA LIMITED
15 Stanhope Gate
London W1Y 6LN
United Kingdom

State of Nationality

GB

State of Residence

GB

Telephone No.

Facsimile No.

Teleprinter No.

2. The International Bureau hereby notifies the applicant that the following change has been recorded concerning:

☐ the person
 ☒ the name
 ☒ the address
 ☐ the nationality
 ☐ the residence

Name and Address

SYNGENTA LIMITED
Fernhurst
Haselmere
Surrey GU27 3JE
United Kingdom

State of Nationality

GB

State of Residence

GB

Telephone No.

Facsimile No.

Teleprinter No.

3. Further observations, if necessary:

This is only a change of name and address. No transfer of patent or other rights has occurred. Agent's address has also been changed accordingly.

4. A copy of this notification has been sent to:

☒ the receiving Office
 ☐ the designated Offices concerned
☐ the International Searching Authority
 ☒ the elected Offices concerned
☒ the International Preliminary Examining Authority
 ☐ other:

The International Bureau of WIPO 34, chemin des Colombettes 1211 Geneva 20, Switzerland Facsimile No.: (41-22) 740.14.35	Authorized officer <p style="text-align: center;">Maria Victoria CORTIELLO</p> Telephone No.: (41-22) 338.83.38
---	--

PATENT COOPERATION TREATY

PCT

NOTIFICATION OF ELECTION

(PCT Rule 61.2)

From the INTERNATIONAL BUREAU

To:

Assistant Commissioner for Patents
United States Patent and Trademark
Office
Box PCT
Washington, D.C. 20231
ETATS-UNIS D'AMERIQUE

in its capacity as elected Office

Date of mailing: 12 October 2000 (12.10.00)	
International application No.: PCT/GB00/01062	Applicant's or agent's file reference: PPD 50391/WO
International filing date: 21 March 2000 (21.03.00)	Priority date: 01 April 1999 (01.04.99)
Applicant: CUTLER, Julia, Lynne et al	

1. The designated Office is hereby notified of its election made:

☒ in the demand filed with the International preliminary Examining Authority on:
01 September 2000 (01.09.00)☐ in a notice effecting later election filed with the International Bureau on:
_____2. The election ☒ was
☐ was not

made before the expiration of 19 months from the priority date or, where Rule 32 applies, within the time limit under Rule 32.2(b).

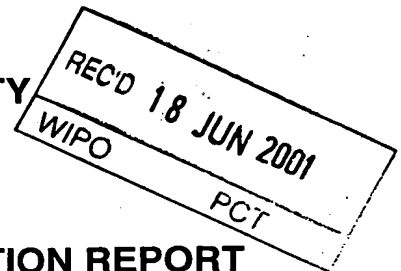
The International Bureau of WIPO 34, chemin des Colombettes 1211 Geneva 20, Switzerland Facsimile No.: (41-22) 740.14.35	Authorized officer: J. Zahra Telephone No.: (41-22) 338.83.38
---	---

PATENT COOPERATION TREATY

PCT

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)



14

Applicant's or agent's file reference PPD 50391/WO		FOR FURTHER ACTION See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416)	
International application No. PCT/GB00/01062	International filing date (day/month/year) 21/03/2000	Priority date (day/month/year) 01/04/1999	
International Patent Classification (IPC) or national classification and IPC A01N25/30			
Applicant SYNGENTA LIMITED et al			

1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.



2. This REPORT consists of a total of 5 sheets, including this cover sheet.

☒ This report is also accompanied by ANNEXES, i.e. sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).

These annexes consist of a total of 3 sheets.

3. This report contains indications relating to the following items:

- I ☒ Basis of the report
- II ☐ Priority
- III ☐ Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
- IV ☐ Lack of unity of invention
- V ☒ Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
- VI ☐ Certain documents cited
- VII ☒ Certain defects in the international application
- VIII ☐ Certain observations on the international application

Date of submission of the demand 01/09/2000	Date of completion of this report 15.06.2001
Name and mailing address of the international preliminary examining authority:  European Patent Office - P.B. 5818 Patentlaan 2 NL-2280 HV Rijswijk - Pays Bas Tel. +31 70 340 - 2040 Tx: 31 651 epo nl Fax: +31 70 340 - 3016	Authorized officer Fort, M Telephone No. +31 70 340 4123 

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No. PCT/GB00/01062

I. Basis of the report

1. With regard to the **elements** of the international application (*Replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report since they do not contain amendments (Rules 70.16 and 70.17)*):

Description, pages:

1-12 as originally filed

Claims, No.:

1-16 as received on 26/02/2001 with letter of 26/02/2001

2. With regard to the **language**, all the elements marked above were available or furnished to this Authority in the language in which the international application was filed, unless otherwise indicated under this item.

These elements were available or furnished to this Authority in the following language: , which is:

- ☐ the language of a translation furnished for the purposes of the international search (under Rule 23.1(b)).
- ☐ the language of publication of the international application (under Rule 48.3(b)).
- ☐ the language of a translation furnished for the purposes of international preliminary examination (under Rule 55.2 and/or 55.3).

3. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international preliminary examination was carried out on the basis of the sequence listing:

- ☐ contained in the international application in written form.
- ☐ filed together with the international application in computer readable form.
- ☐ furnished subsequently to this Authority in written form.
- ☐ furnished subsequently to this Authority in computer readable form.
- ☐ The statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.
- ☐ The statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished.

4. The amendments have resulted in the cancellation of:

- ☐ the description, pages:
- ☐ the claims, Nos.:
- ☐ the drawings, sheets:

5. ☒ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)):

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No. PCT/GB00/01062

(Any replacement sheet containing such amendments must be referred to under item 1 and annexed to this report.)
see separate sheet

6. Additional observations, if necessary:

V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Yes: Claims 1-16
	No: Claims
Inventive step (IS)	Yes: Claims 1-16
	No: Claims
Industrial applicability (IA)	Yes: Claims 1-16
	No: Claims

2. Citations and explanations **see separate sheet**

VII. Certain defects in the international application

The following defects in the form or contents of the international application have been noted:
see separate sheet

**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT - SEPARATE SHEET**

International application No. PCT/GB00/01062

Re Item I

Basis of the report

The preferred compounds of formula (I) (original claim 2) correspond to combinations of preferred groups R1, R2, R3, R4 and X, wherein the preferred R4 group is an alkyl group containing **2-3 carbon atoms**. The definition of R4 as an alkyl group containing **1-4 carbon atoms** in the newly filed claim 1 where R1, R2, R3 and X are the groups defined in original claim 2 (see also p.3 of the description as originally filed) is considered to go beyond the disclosure as filed. Therefore this report has been established on the basis of the amended claims with the exception that in the newly filed claim 1, the group R4 is considered to represent an alkylene group containing from 2-3 carbon atoms.

Re Item V

Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

The newly filed claim 1 has been limited to compounds of formula (I) wherein R1 and R2 are independently hydrogen or a lower alkyl group and X represents one of the groups (IA), (IB) and (IC) as defined in amended claim 1 with the proviso that the compound of formula (I) is not Jeffamine D-230.

The claimed compounds of formula (I) wherein X represents IA no longer include the compounds having three alkoxyated groups attached to the nitrogen described in each of D2-D3 (D2= WO 96/32839 and D3= WO97/324769).

The objection as to lack of novelty of the diamine compounds corresponding to X= IB is not maintained since the compositions comprising Jeffamine D-230 as adjuvant which have been described in D1 (D1= EP 0 375 624) are excluded by the use of a proviso. Thus the subject-matter of the newly filed claims is novel vis-à-vis the prior art cited in the search report.

The subject-matter of the newly filed claims can also be considered as being inventive for the following reasons:

It is known from D2, which is considered to represent the closest prior art, that the use of a tertiary etheramine surfactant having three alkoxyated groups attached to the

**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT - SEPARATE SHEET**

International application No. PCT/GB00/01062

nitrogen, improves the herbicidal activity of glyphosate formulations.

Given this prior art, the problem underlying the present invention may be seen as providing further adjuvants capable of improving the activity of agrochemicals.

As can be seen from the description and examples, the adjuvants according to the amended claim 1 provide excellent enhancement of herbicidal activity. In view of the structural differences between the claimed compounds of formula (I) and the etheramine surfactants described in D2, the aforementioned improvement could not be predicted.

As to document D1, it relates to a different problem, i.e. reducing the volatility of biologically active compounds but does not describe any improvement of herbicidal activity obtained by the addition of the surfactants described therein.

Thus the subject-matter of the newly filed claims 1-16 can be considered as being inventive.

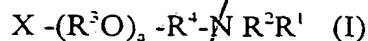
Re Item VII

Certain defects in the international application

The description has not been brought into conformity with the newly filed claims, contrary to the requirements of Article 6 PCT.

Claims

1. An agrochemical composition comprising an agrochemical active ingredient and an adjuvant of formula (I) and salts thereof



wherein R^1 and R^2 are independently hydrogen or a lower alkyl group or a group $X'-(R^3O)_a-R^4$ - wherein R^3 and R^4 respectively may take any of the values of R^3 and R^4 as hereinafter defined and wherein X' is -OH or a lower alkoxy group containing from 1 to 6 carbon atoms and a' is from 0 to 400

R^3O is an ethoxy, propoxy or butoxy group or a random or block mixture thereof, R^4 is a linear or branched chain alkylene bridging group containing from 1 to 4 carbon atoms, X is

(IA) -OH or a lower alkoxy group containing from 1 to 6 carbon atoms or X is

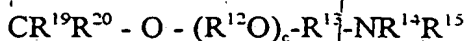
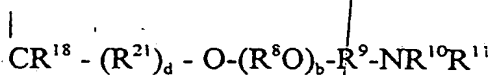
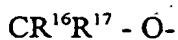
(IB) a group R^5R^6N - or $R^5R^6N-R^7$ -

wherein R^5 and R^6 are independently hydrogen or a lower alkyl group or a group $X'-(R^3O)_a-R^4$ - as hereinbefore defined wherein X' is -OH or a lower alkoxy group containing from 1 to 6 carbon atoms,

and R^7 is a linear or branched chain alkylene bridging group containing from 1 to 4 carbon atoms

or X is

(IC) a group



wherein R^{10} , R^{11} , R^{14} and R^{15} are independently hydrogen or a lower alkyl group or a group $X'-(R^3O)_a-R^4$ - as hereinbefore defined wherein X' is -OH or a lower alkoxy group containing from 1 to 6 carbon atoms,

Replaced by Article 34

and R^8 and R^{12} are independently alkyl groups containing from 1 to 4 carbon atoms and R^9 , R^{13} and R^{21} are independently a linear or branched chain alkylene bridging group containing from 1 to 6 carbon atoms, R^{16} , R^{17} , R^{18} , R^{19} and R^{20} are independently hydrogen or a lower alkyl group and d is 0 or 1

and wherein a, is from 1 to 400 or if X is of formula IC, the sum of a, b and c is from 3 to 400.

2. A composition according to claim 1 wherein

X is -OH or a lower alkoxy group containing from 1 to 4 carbon atoms or

X is R^5R^6N - wherein R^5 and R^6 are hydrogen or a lower alkyl group containing from 1 to 4 carbon atoms or

X is a group of formula IC'

$CH_2 - O -$

$|$
 $CR^{18} - (R^{21})_d - O - (R^8O)_b - R^9 - NH_2$

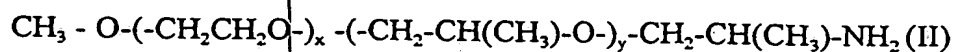
$|$
 $CH_2 - O - (R^{12}O)_c - R^{13} - NH_2$

wherein R^8O and $R^{12}O$ are independently ethoxy, or propoxy or a random or block mixture thereof, R^9 and R^{13} are independently a linear or branched chain alkylene bridging group containing 2 or 3 carbon atoms, R^{21} is a linear or branched chain alkylene bridging group containing from 1 to 3 carbon atoms, R^{18} is hydrogen or lower alkyl containing from 1 to 4 carbon atoms, d is 0 or 1,

R^1 and R^2 are independently hydrogen or a lower alkyl group containing from 1 to 4 carbon atoms, R^3O is ethoxy, or propoxy or a random or block mixture thereof, R^4 is a linear or branched chain alkylene bridging group containing 2 or 3 carbon atoms and a is from 1 to 400 or if X is of formula IC', the sum of a, b and c is from 3 to 400.

3. A composition according to claim 1 or 2 wherein a is from 1 to 50 or if X is of formula IC or IC' respectively, the sum of a, b and c is from 3 to 90 and wherein in the group $X' - (R^3O)_a - R^4 -$ if present, a' is from 0 to 50.

4. A composition according to claim 1 wherein the adjuvant of formula (I) is an alkoxyated monoamine, having the formula II



wherein the average degree of ethoxylation (x) is from 0 to about 45 and the average degree of propoxylation (y) is from 0 to about 90 provided that x and y are not both 0 at the same time.

5. A composition according to claim 4 wherein the value of x is from 0 to about 20 and of y is from about 2 to about 30.

6. A composition according to claim 1 wherein the compound of formula (I) is a diamine having a formula (II)



wherein w is an average of from about 1 to about 80.

7. A composition according to claim 6 wherein w is an average of from about 2 to about 35

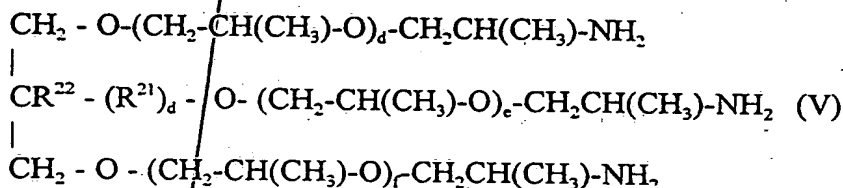
8. A composition according to claim 1 wherein the compound of formula (I) is a diamine having a formula (IV)



wherein the sum of r + t is an average of from 1 to 20 propoxy groups and s is an average of from 2 to 50 ethoxy units.

9. A composition according to claim 8 wherein the sum of r + t is from about 2 to about 15 and s is from about 3 to about 20.

10. A composition according to claim 1 wherein the compound of formula (I) is a propoxylated triamine having the formula (V)



wherein the sum of d + e + f is an average of from about 5 to 90, R²² is hydrogen or lower alkyl containing 1 to 4 carbon atoms, R²¹ is a linear or branched chain alkylene bridging group containing 1 to 3 carbon atoms and d is 0 or 1.

11. A composition according to any of the preceding claims wherein the proportion of adjuvant of formula (I) to the agrochemical is from 1:20 to 3:1 by weight.

12. A composition according to any of the preceding claims wherein the adjuvant of formula (I) in claim 1 is used in combination with an alkylpolyglycoside surfactant.

13. A composition according to claim 12 wherein the ratio of the adjuvant of formula (I) to the alkylpolyglycoside surfactant is from 1 : 40 to 4 : 1.
14. A composition according to any of the preceding claims wherein the agrochemical active ingredient is a salt of glyphosate, a salt of fomesafen or a paraquat salt.
- 5 15. A composition according to any of claims 1 to 13 wherein the adjuvant of formula (I) in claim 1 is used in the form of a salt with glyphosate or a salt with an acidic surfactant.
16. A process of severely damaging or killing unwanted plants which process comprises applying to the plants or to the growth medium of the plants, a herbicidally effective
10 amount of a composition as claimed in claim 14.
17. A composition according to any of claims 1 to 15 which is an aqueous composition containing from 0.01% to 90% by weight of the active ingredient.



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁷ : A01N 25/30, 57/20	A1	(11) International Publication Number: WO 00/59302 (43) International Publication Date: 12 October 2000 (12.10.00)
(21) International Application Number: PCT/GB00/01062 (22) International Filing Date: 21 March 2000 (21.03.00) (30) Priority Data: 9907669.7 1 April 1999 (01.04.99) GB (71) Applicant (for all designated States except US): ZENECA LIMITED [GB/GB]; 15 Stanhope Gate, London W1Y 6LN (GB). (72) Inventors; and (75) Inventors/Applicants (for-US only): CUTLER, Julia, Lynne [GB/GB]; Jealotts Hill International Research Centre, Bracknell, Berkshire RG42 6ET (GB). BEAN, Michael, John [GB/GB]; Jealotts Hill International Research Centre, Bracknell, Berkshire RG42 6ET (GB). SEVILLE, Antony, George [GB/GB]; Jealotts Hill International Research Centre, Bracknell, Berkshire RG42 6ET (GB). (74) Agents: RICKS, Michael, James et al.; Zeneca Agrochemicals, Intellectual Property Dept., P.O. Box 3538, Jealott's Hill Research Station, Bracknell RG42 6YA (GB).		(81) Designated States: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, DE, DK, DM, DZ, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i>
(54) Title: AGROCHEMICAL COMPOSITION $ \begin{array}{c} \text{CR}^{16}\text{R}^{17} - \text{O}- \\ \\ \text{CR}^{18} - (\text{R}^{21})_d - \text{O} - (\text{R}^8\text{O})_b - \text{R}^9 - \text{NR}^{10}\text{R}^{11} \\ \\ \text{CR}^{19}\text{R}^{20} - \text{O} - (\text{R}^{12}\text{O})_c - \text{R}^{13} - \text{NR}^{14}\text{R}^{15} \end{array} \quad (1) $ (57) Abstract <p>An aqueous agrochemical composition comprises an agrochemical active ingredient such as glyphosate, paraquat or fomesafen and an adjuvant of formula (I): $\text{X}-(\text{R}^3\text{O})_a-\text{R}^4-\text{N R}^2\text{R}^1$ and salts thereof, wherein R^1 and R^2 are independently hydrogen or a lower alkyl group or a group $\text{X}-(\text{R}^3\text{O})_a-\text{R}^4-$ wherein X is $-\text{OH}$ or a lower alkoxy group; R^3O is an ethoxy, propoxy or butoxy group or a random or block mixture thereof; R^4 is a linear or branched chain alkylene bridging group containing from 1 to 4 carbon atoms; X is (IA) $-\text{OH}$ or a lower alkyloxy group; or (IB) a group $\text{R}^5\text{R}^6\text{N}-$ or $\text{R}^5\text{R}^6\text{N}-\text{R}^7-$; or (IC) a group (1) wherein a, is from 1 to 400 or if X is of formula IC, the sum of a, b and c is from 3 to 400 and d is 0 or 1.</p>		

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

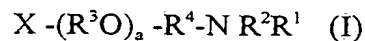
AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav	TM	Turkmenistan
BF	Burkina Faso	GR	Greece		Republic of Macedonia	TR	Turkey
BG	Bulgaria	HU	Hungary	ML	Mali	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MN	Mongolia	UA	Ukraine
BR	Brazil	IL	Israel	MR	Mauritania	UG	Uganda
BY	Belarus	IS	Iceland	MW	Malawi	US	United States of America
CA	Canada	IT	Italy	MX	Mexico	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NE	Niger	VN	Viet Nam
CG	Congo	KE	Kenya	NL	Netherlands	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NO	Norway	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's	NZ	New Zealand		
CM	Cameroon		Republic of Korea	PL	Poland		
CN	China	KR	Republic of Korea	PT	Portugal		
CU	Cuba	KZ	Kazakstan	RO	Romania		
CZ	Czech Republic	LC	Saint Lucia	RU	Russian Federation		
DE	Germany	LI	Liechtenstein	SD	Sudan		
DK	Denmark	LK	Sri Lanka	SE	Sweden		
EE	Estonia	LR	Liberia	SG	Singapore		

AGROCHEMICAL COMPOSITION

This invention relates to an agrochemical composition and in particular to an agrochemical composition containing an activity-enhancing adjuvant.

5 An agrochemical is generally used with an adjuvant or combination of adjuvants to provide optimum biological activity. Much has been published on the selection of adjuvants to achieve particular effects with individual agrochemicals and classes of agrochemical. In general it has been assumed that activity-enhancement results from surfactant properties of the adjuvant and most such activity-enhancing adjuvants are surfactants in that they contain
10 within the molecule both a hydrophobic portion and a lypophobic portion. We have now found that a class of alkoxyated amines provides excellent activity enhancement when used in an agrochemical formulation. Surprisingly certain members of the class have either no surfactant properties or low surfactant properties. Furthermore, unlike many surfactants used as conventional agrochemical adjuvants, the alkoxyated amines of the present
15 invention generally exhibit an exceptionally low toxicological profile and in particular excellent ecotoxicological characteristics and provide compositions which are especially benign to the environment. It is exceptional to find adjuvants which combine a high level of activity enhancement with low toxicity.

According to the present invention there is provided an agrochemical composition
20 comprising an agrochemical active ingredient and an adjuvant of formula (I) and salts thereof



25 wherein R^1 and R^2 are independently hydrogen or a lower alkyl group or a group $X'-(R^3O)_a-R^4$ - wherein R^3 and R^4 respectively may take any of the values of R^3 and R^4 as hereinafter defined and wherein X' is -OH or a lower alkoxy group containing from 1 to 6 carbon atoms and a is from 0 to 400

R^3O is an ethoxy, propoxy or butoxy group or a random or block mixture thereof,
30 R^4 is a linear or branched chain alkylene bridging group containing from 1 to 4 carbon atoms, X is

(IA) -OH or a lower alkoxy group containing from 1 to 6 carbon atoms

or X is

(IB) a group R^5R^6N- or $R^5R^6N-R^7-$

wherein R^5 and R^6 are independently hydrogen or a lower alkyl group or a group $X'-(R^3O)_a-R^4-$ as hereinbefore defined wherein X' is -OH or a lower alkoxy group

5 containing from 1 to 6 carbon atoms,

and R^7 is a linear or branched chain alkylene bridging group containing from 1 to 4 carbon atoms

or X is

(IC) a group

10

$CR^{16}R^{17}-O-$

$|$
 $CR^{18}-(R^{21})_d-O-(R^8O)_b-R^9-NR^{10}R^{11}$

15

$|$
 $CR^{19}R^{20}-O-(R^{12}O)_c-R^{13}-NR^{14}R^{15}$

wherein R^{10} , R^{11} , R^{14} and R^{15} are independently hydrogen or a lower alkyl group or a group $X'-(R^3O)_a-R^4-$ as hereinbefore defined wherein X' is -OH or a lower alkoxy group containing from 1 to 6 carbon atoms,

20

and R^8 and R^{12} are independently alkyl groups containing from 1 to 4 carbon atoms and R^9 and R^{13} and R^{21} are independently a linear or branched chain alkylene bridging group containing from 1 to 6 carbon atoms, R^{16} , R^{17} , R^{18} , R^{19} and R^{20} are independently hydrogen or a lower alkyl group and d is 0 or 1

25

and wherein a, is from 1 to 400 or if X is of formula IC, the sum of a, b and c is from 3 to 400.

A considerable number of salts of the compound of formula (I) suitable for use in agrochemical applications will occur to one skilled in the art. Examples of salts include phosphate, sulphate, carboxylate, acetate, formate and chloride although many other suitable salts will occur to one skilled in the art. Alternatively the compound of formula (I) may

30 form a salt with an acidic agrochemical such as glyphosate. Salts of the compound of formula (I) can also be prepared from acidic surfactants, for example optionally ethoxylated alkyl or alkylene ester derivatives of phosphoric acid or phosphonic acid, or optionally ethoxylated alkyl or alkylene carboxylic acids or sulphonic acids. It will be appreciated that where more than one amine functionality is present in the compound of formula (I) or the

relevant acid has more than one functional group, the option for different salt stoichiometries and mixed salts exists and all such variations are included herein.

As used herein, the term lower alkyl means a linear or branched chain primary or secondary alkyl group containing from 1 to 6 carbon atoms. Preferred lower alkyl groups contain from 1 to 4 carbon atoms, and methyl, ethyl and propyl or isopropyl groups are especially preferred.

$R^1, R^2, R^5, R^6, R^{10}, R^{11}, R^{14}$ and R^{15} are preferably methyl or hydrogen. Hydrogen is especially preferred.

Thus it is preferred that in a compound of formula (I):-

10 X is -OH or a lower alkoxy group containing from 1 to 4 carbon atoms or
X is R^5R^6N - wherein R^5 and R^6 are hydrogen or a lower alkyl group containing from 1 to 4 carbon atoms or
X is a group of formula IC'

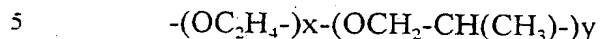
15 $CH_2 - O -$
|
 $CR^{18} - (R^{21})_d - O - (R^8O)_b - R^9 - NH_2$
|
 $CH_2 - O - (R^{12}O)_c - R^{13} - NH_2$

20 wherein R^8O and $R^{12}O$ are independently ethoxy, or propoxy, in particular isopropoxy, or a random or block mixture thereof, R^9 and R^{13} are independently a linear or branched chain alkylene bridging group containing 2 or 3 carbon atoms and R^{21} is a linear or branched chain alkylene bridging group containing from 1 to 3 carbon atoms, R^{18} is hydrogen or lower alkyl containing from 1 to 4 carbon atoms and d is 0 or 1,

25 R^1 and R^2 are independently hydrogen or a lower alkyl group containing from 1 to 4 carbon atoms, R^3O is ethoxy, or propoxy, in particular isopropoxy, or a random or block mixture thereof, R^4 is a linear or branched chain alkylene bridging group containing 2 or 3 carbon atoms and a is from 1 to 400 or if X is of formula IC', the sum of a, b and c is from 3 to 400.

The compounds for use in the composition of the present invention are alkoxyated
30 monoamines (X is of Formula IA), diamines (X is of Formula IB) or triamines (X is of Formula IC). Alkoxylation typically takes place to introduce ethoxy groups or propoxy groups, although butoxy groups may sometimes also be used. The propoxy group is preferably an isopropoxy group, $-OCH_2-CH(CH_3)-$. Mixed alkoxylation may also take place to introduce for example both ethoxy and propoxy or butoxy groups which may be present

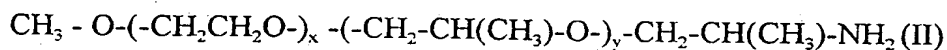
as a mixture in either random or block arrangement. Thus each of $-(OR^3)_a-$, $-(OR^8)_b-$ and $-(OR^{12})_c-$ in the above formulae independently represent alkoxy groups, for example ethoxy and propoxy groups or a mixture thereof. Thus the definition of group $-(OR^3)_a$ for example includes a group



wherein a is represented by the sum of x and y. Other combinations of for example ethoxy propoxy and butyloxy groups in any desired order are similarly included in the definition of $-(OR^3)_a-$, $-(OR^8)_b-$ and $-(OR^{12})_c-$ respectively.

The process of alkoxylation may produce a mixture of products having different
 10 degrees of alkoxylation. Thus the values of a, b, c and a' represent an average degree of alkoxylation over the product as a whole. Preferred values of a, b, and c, respectively are from 1 to 100, for example from 1 to 50 and especially from 1 to 30. Thus when X in formula (I) is of formula IC, the sum of $a + b + c$ is preferably from 3 to 90. In the group $X'-(R^3O)_a-R^4-$ if present, a' is preferably from 0 to 50 and especially from 0 to 30.

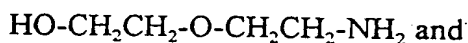
15 An especially preferred alkoxyated monoamine (wherein X is of formula IA) for use in the present invention has the formula II wherein X is methoxy, $-(R^3O)_a$ represents a mixture of ethoxy and propoxy groups R^4 represents a propylene bridging group:-



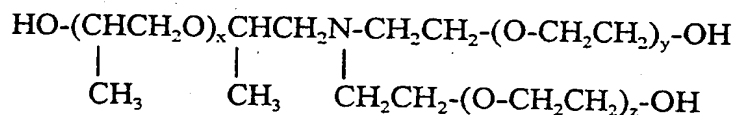
The average degree of ethoxylation (x) may vary from 0 to about 45 or more preferably
 20 from 0 to about 40, for example from 0 to about 20 and the average degree of propoxylation (y) may vary from 0 to about 90 and more preferably from about 1 to about 35, for example from about 2 to about 30, provided that x and y are not both 0 at the same time. Products are commercially available wherein x is about 1 and y is about 9; x is about 19 and y is about 3; x is about 6 and y is about 29 and x is about 32 and y is about 10. As specific
 25 examples of commercially available products there may be mentioned JEFFAMINE M600 (JEFFAMINE is a trade mark of Huntsman Limited) having an approximate molecular weight of 600 and a propoxy to ethoxy ratio of 9 to 1, JEFFAMINE M1000 having an approximate molecular weight of 1000 and a propoxy to ethoxy ratio of 3 to 19, JEFFAMINE M2005 having an approximate molecular weight of 2000 and a propoxy to
 30 ethoxy ratio of 29 to 6 and JEFFAMINE M2070 having an approximate molecular weight of 2000 and a propoxy to ethoxy ratio of 10 to 32.

Also included in the scope of the present invention is

(i) diethylene glycolamine wherein in Formula I, X is OH, (R³O) is ethoxy, a is 1 and R⁴ is an ethylene bridging group and R¹ and R² are hydrogen:-

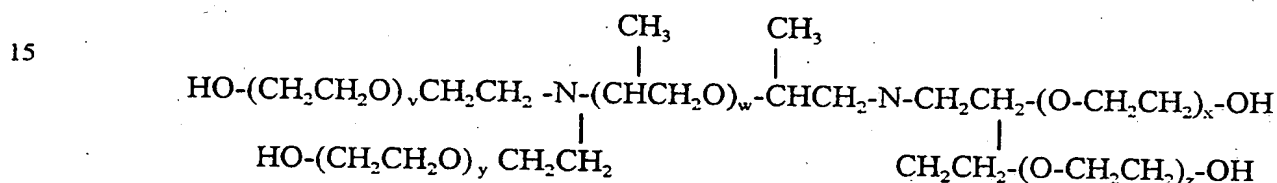


5 (ii) a compound of formula



10 wherein in Formula I, X is -OH, R³ and R⁴ are isopropyl, R¹ and R² are X'-(R³O)_a-R⁴-, X' is -OH, R³ and R⁴ are ethyl and x, y and z respectively take any of the values defined for a or a' as the case may be and

(iii) a compound of formula

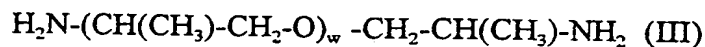


15 wherein in Formula I, X is R⁵R⁶N-, R³ and R⁴ are isopropyl, R¹, R², R⁵ and R⁶ are X'-(R³O)_a-R⁴-, X' is -OH, R³ and R⁴ are ethyl and v, w, x, y and z respectively take any of the values defined for a or a' as the case may be.

Also included in the scope of the present invention is

tris 2-(2-methoxyethoxy)ethylamine wherein in formula I, X is OCH₃, (R³O) is ethoxy, a is 1 and R⁴ is an ethylene bridging group and wherein R¹ and R² are each a group -R⁴-(OR³)_a-X' wherein (R³O) is ethoxy, a' is 1, R⁴ is an ethylene bridging group and X' is OCH₃.

25 An especially preferred propoxylated diamine (wherein X is of formula IB) for use in the present invention has the formula III wherein X is a group H₂N-, -(R³O-)_a represents propoxy groups R⁴ represents a propoxy bridging group:-



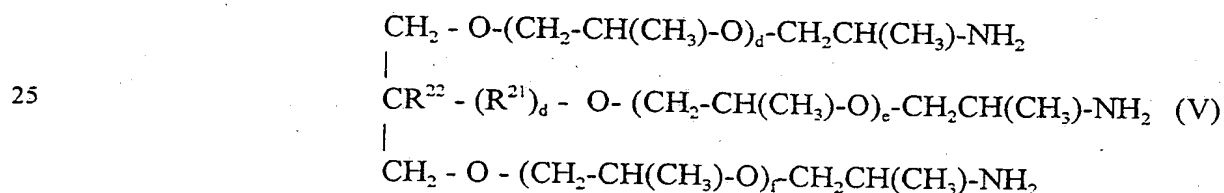
30 wherein w is an average of from about 1 to about 80. Products are commercially available wherein w is an average of about 2.6, 5.6, 33.1 and 68. As Examples of commercially available products of formula III, there may be mentioned JEFFAMINE D230 having an approximate molecular weight of 230 and a value of w of about 2.6, JEFFAMINE D400 having an approximate molecular weight of 400 and a value of w of about 5.6,

35 JEFFAMINE D2000 having an approximate molecular weight of 2000 and a value of w of

about 33.1, and JEFFAMINE D4000 having an approximate molecular weight of 4000 and a value of w of about 68. An especially preferred value for w is from about 2 to about 35, for example from about 2 to about 30.

An alternative diamine (wherein X is of formula IB) having a mixture of
 5 ethoxylation and propoxylation for use in the present invention has the formula IV wherein X is a group H_2N- , $-(R^3O-)_s$ represents a mixture of ethoxy and propoxy groups R^1 and R^2 are hydrogen and R^4 represents a propylene bridging group:-
 $H_2N-(CH(CH_3)-CH_2-O)_r-(CH_2CH_2-O)_s-(CH_2-CH(CH_3)-O)_t-CH_2-CH(CH_3)-NH_2$ (IV)
 wherein the sum of $r + t$ (total propoxy content) is an average of from 1 to 20 propoxy
 10 groups, for example from about 1 to 10 propoxy units and s is an average of from 2 to 50 for example from 5 to 50 ethoxy units. Commercial products are available wherein the sum of $r + t$ is about 3.6 and s represents an average of about 9, or 15.5 respectively or wherein $r + t$ is about 6 and s represents an average of about 38.7. As examples of commercially available products of formula (IV) there may be mentioned JEFFAMINE ED 600 having an
 15 approximate molecular weight of 600 and an propoxy to ethoxy ratio of 3.6 to 9, JEFFAMINE ED 900 having an approximate molecular weight of 900 and an propoxy to ethoxy ratio of 3.6 to 15.5 and JEFFAMINE ED 2003 having an approximate molecular weight of 2000 and an propoxy to ethoxy ratio of 6.0 to 38.7. It is especially preferred that the value of $(r + t)$ is from about 2 to about 15 and s is from about 3 to about 20.

20 An especially preferred propoxylated triamine (wherein X is formula IC) has the formula (V)



wherein the sum of $d + e + f$ is an average of from about 5 to 90 and R^{22} is hydrogen or
 30 lower alkyl containing 1 to 4 carbon atoms such as methyl or ethyl, R^{21} is a linear or branched chain alkylene bridging group containing from 1 to 3 carbon atoms and d is 0 or 1. Products are available commercially wherein the sum of $d + e + f$ is about 5.6, about 50 and about 85 respectively. Thus as examples of commercially available products of formula (V) there may be mentioned JEFAMINE T403 having an approximate molecular weight of 440

and a value of $d + e + f$ (total propoxy content) of 5.6, JEFAMINE T3000 having an approximate molecular weight of 3000 and a value of $d + e + f$ (total propoxy content) of 50 and JEFAMINE T5000 having an approximate molecular weight of 5000 and a value of $d + e + f$ (total propoxy content) of 85.

5 We have found that the activity enhancing effect of the adjuvants in the composition of the present invention is particularly and surprisingly marked when the agrochemical active ingredient is water-soluble. The agrochemical for use in the composition of the present invention is preferably a water-soluble electrolyte such as an agrochemical salt and in particular a herbicidally active agrochemical salt for example a salt of glyphosate,
10 paraquat or fomesafen. Typical of the commonly available salts of glyphosate are the isopropylamine, trimethylsulphonium, sodium, potassium, ammonium, and ethanolamine salts. Paraquat is generally sold in the form of paraquat dichloride. Fomesafen is generally formulated as the sodium salt.

The proportion of adjuvant of formula (I) to agrochemical, for example glyphosate
15 (expressed as the acid) may vary within wide ranges depending on the desired level of activation. Typically the proportion of adjuvant of formula (I) to agrochemical will be from 1:40 to 3:1 for example from 1:20 to 3:1 by weight and especially from 1:10 to 1:1 by weight.

The compositions of the present invention may be used on their own but are
20 preferably used in the form of a composition containing a carrier comprising a solid or liquid diluent.

Compositions of the invention include both dilute compositions, which are ready for immediate use, and concentrated compositions, which require to be diluted before use, usually with water. The concentration of the composition will depend on the nature of the
25 active ingredient. Typically, and especially for example if the active ingredient is a herbicide, the compositions contain from 0.01% to 90% by weight of the active ingredient. Dilute compositions ready for use preferably contain from 0.01 to 2% of active ingredient, while concentrated compositions may contain from 20 to 90% of active ingredient, although from 20 to 70% is usually preferred.

30 The solid compositions may be in the form of granules, or dusting powders wherein the active ingredient and adjuvant are mixed with a finely divided solid diluent, e.g. kaolin, bentonite, kieselguhr, dolomite, calcium carbonate, talc, powdered magnesia, Fuller's earth

and gypsum. In some instances, and in particular when the active ingredient is glyphosate, inorganic salts such as ammonium sulphate may be used both as adjuvant and solid support. They may also be in the form of dispersible powders or grains, comprising a wetting agent to facilitate the dispersion of the powder or grains in liquid. Solid compositions in the form of a powder may be applied as foliar dusts.

The rate of application of the compositions of the invention will depend on a number of factors depending in particular on the nature of the active ingredient. When the active ingredient is a herbicide, such factors include, the compound chosen for use, the identity of the plants whose growth is to be inhibited, the formulations selected for use and whether the compound is to be applied for foliage or root uptake. As a general guide, however, an application rate of from 0.001 to 20 kilograms active ingredient per hectare is suitable while from 0.025 to 10 kilograms per hectare may be preferred.

The adjuvant of formula (I) or a mixture of different adjuvants of formula (I) may be used as the sole adjuvant to enhance the biological activity or physical properties of the agrochemical or may alternatively be used in conjunction with one or more additional adjuvants. The adjuvant of formula (I) may for example be combined with cationic surfactants, anionic surfactants, amphoteric surfactants or non-ionic surfactants. Such surfactants are well known in the art but as surfactants which are particularly well suited to be combined with an adjuvant of formula (I) there may be mentioned alkyl glycosides (mono and poly), alcohol ethoxylates, alkyl phenol ethoxylates, alkyl ester ethoxylates, sorbitan ester ethoxylates, siloxane ethoxylates, acetylenic diol ethoxylates, optionally alkoxyated tertiary or quaternary alkyl amines, optionally alkoxyated alkyl amine oxides, alkyl betaines optionally alkoxyated alkyl phosphate esters and sucrose alkyl esters. The adjuvant of formula (I) may also be combined with other activity-enhancing adjuvants, for example ammonium sulphate, urea or humectants, such as glycerol, polyethylene glycol, sorbitol, ethylene glycol, propylene glycol and lactate salts.

Certain of the adjuvants for use in the composition of the present invention have surprisingly low surface activity (high surface tension) as compared with conventional agrochemical adjuvants. These adjuvants with low surface activity generally exhibit a more favourable toxicological profile. Surface tension of the adjuvants for use in the present invention was measured as a 0.2% w/v solution in deionised water adjusted to pH 4 with hydrochloric acid at 20°C, and preferred adjuvants such as JEFFAMINE ED600 ED900 and

D400 have a surface tension measured by this method of greater than 50 mNm^{-1} as compared with AGRIMUL PG2067 alkylpolyglycoside which has a surface tension measured by this method of 28 mNm^{-1} . Adjuvants having a surface tension of less than 50 mNm^{-1} also give excellent results and JEFFAMINE D2000 for example having a surface tension measured by this method of 42 mNm^{-1} may even provide advantages on certain weed species as discussed below.

Compositions of the present invention generally exhibit excellent low-foaming properties when the composition is incorporated in the spray tank and during transportation and spraying.

When the active ingredient is a herbicide and in particular a water-soluble herbicide, adjuvants of formula (I) generally provide excellent and effective enhancement of activity in respect of most important weed species encountered in the field. Enhancement may however be less marked on certain "difficult" weed species. We have found that the use of a mixture of an adjuvant of formula (I) with a surfactant and in particular with an alkylpolyglycoside surfactant may provide excellent enhancement of activity both against normal weed species and against "difficult" species. Indeed in certain circumstances synergy may be observed and greater enhancement of control of "difficult" species may be obtained than when using either the adjuvant of formula (I) or the alkylpolyglycoside alone. The ratio of the adjuvant of formula (I) to the alkylglycoside is preferably from 1 : 40 to 4 : 1, for example 1 : 20 to 4 : 1, especially from 1 : 6 to 2 : 1 and most preferably about 1 to 1.

When the active ingredient is a herbicide, the invention provides, in a further aspect, a process for severely damaging or killing unwanted plants, which process comprises applying to the plants, or to the growth medium of the plants, a herbicidally effective amount of a composition as hereinbefore defined.

The invention is illustrated by the following Examples in which all parts and percentages are by weight unless otherwise stated.

Examples 1 to 10

Potassium glyphosate was applied at 500g glyphosate acid equivalent/ha to *Abutilon theophrasti* (ABUTH) plants grown in the glass-house. All treatments were made up in deionised water and applied using a tracksprayer with a 11002 nozzle at a spray application volume of 200l/ha. All treatments were replicated 4 times. After spraying the plants were

laid out in a glass-house and maintained at a temperature of 24°C by day and 19°C by night. The JEFFAMINE adjuvants were used in a proportion 0.2% w/v. A visual assessment of % control, where 0=unaffected and 100=complete kill, was carried out 16 days after treatment.

Example No	Treatment	% control
Comparison	No adjuvant	37
1	JEFFAMINE D400	93
2	JEFFAMINE D2000	76
3	JEFFAMINE T3000	79
4	JEFFAMINE ED600	89
5	JEFFAMINE ED900	85
6	JEFFAMINE ED2003	85
7	JEFFAMINE M600	85
8	JEFFAMINE M1000	81
9	JEFFAMINE M2005	70
10	JEFFAMINE M2070	74

EXAMPLES 11 TO 14

Potassium glyphosate was applied to *Abutilon theophrasti* (ABUTH), *Brassica napus* (BRSNS) and *Veronica persica* (VERPE) drilled as rows in the field, at a spray application volume of 200l/ha. The indicated adjuvant was included in the formulation at a total adjuvant concentration of 0.2% w/v. Application rates were 150, 300 and 450 g glyphosate acid/ha and each treatment was replicated 3 times. Data (mean of the three replicates and across all rates) is presented for a visual assessment of % control carried out at 26 days after application (DAA), where 0 = unaffected and 100% = complete kill.

AL2042 is an alkylpolyglycoside surfactant based on the same alkylpolyglycoside as AGRIMUL PG 2067. Both JEFFAMINE ED600 and JEFFAMINE D400 showed excellent adjuvant activity on representative species ABUTH and VERPE. On the "difficult" species BRSNS, the combination of the JEFFAMINE adjuvant and the alkylpolyglycoside showed greater activity than either the JEFFAMINE adjuvant or the alkylpolyglycoside on its own.

Example No	Total adjuvant = 0.2%	ABUTH	BRSNS	VERPE
11	JEFFAMINE ED600	70.0	64.7	48.8
12	JEFFAMINE D400	64.9	62.2	47.2
13	JEFFAMINE ED600 and Agrimul PG2067 (0.1% + 0.1%)	57.8	78.9	44.4
14	JEFFAMINE D400 and Agrimul PG2067 (0.1% + 0.1%)	57.7	77.1	44.7
Comparison	AL2042	45.8	70.3	39.7

EXAMPLE 15

This Example illustrates the use of a salt of ethoxy (5 moles of EO).isotridecyl phosphate ester in the acid form (CRODAFOS T5A) with JEFFAMINE ED600.

- 5 CRODAFOS T5A is a mixture of mono and di esters. CRODAFOS is a tradename of Croda Potassium glyphosate, in combination with the adjuvants specified below, was applied to *Ipomoea hederacea* (IPOHE) at 300 g glyphosate acid equivalent/ha. All treatments were made up in deionised water and applied using a tracksprayer with a 11002 nozzle at a spray application volume of 200l/ha. All treatments were replicated 4 times.
- 10 After spraying the plants were laid out in a glass-house and maintained at a temperature of 24°C by day and 19°C by night. A visual assessment of % control was carried out 16 days after treatment

Treatment	IPOHE - % control
No adjuvant	64
AL2042	71
CRODAFOS T5A, JEFFAMINE ED600 salt	86
CRODAFOS T5A, potassium salt	79

15

The AL2042 was applied at 0.2% w/v and the CRODAFOS T5A salts were applied at 0.2% w/v phosphate ester acid equivalent. The Crodafos T5A potassium salt was prepared by neutralising the phosphate ester in its acid form with potassium hydroxide to pH6. The CRODAFOS T5A JEFFAMINE ED600 salt was prepared by neutralising the phosphate ester in its acid form with JEFFAMINE ED600 to pH6.

20

EXAMPLE 16

This Example illustrates the use of salts of glyphosate acid and the adjuvants of Formula (I).

- 5 Glyphosate trimesium and the glyphosate salts of the indicated adjuvants of formula (I) were applied to *Sorghum halepense* (SORHA) at 500, 1000, 2000 and 4000 g glyphosate acid equivalent/ha. All treatments were made up in deionised water and applied using a tracksprayer with a 11002 nozzle at a spray application volume of 200l/ha. All treatments were replicated 3 times. After spraying the plants were laid out in a glass-house and
- 10 maintained at a temperature of 24°C by day and 19°C by night. A visual assessment of % control was carried out 22 days after treatment and calculated doses for 90% control (ED90) were derived. AL2042 alkylpolyglycoside was used at 0.25% w/v as additional surfactant with all treatments. It will be appreciated that a low ED90 value indicates high activity.

Glyphosate salt	Adjuvant	SORHA - ED90 gae/ha
Glyphosate trimesium	AL2042	1410
Glyphosate JEFFAMINE D400	AL2042	821
Glyphosate JEFFAMINE M600	AL2042	493

15

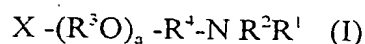
EXAMPLE 17

- Paraquat dichloride, in combination with the adjuvants specified below, was applied to *Abutilon theophrasti* (ABUTH) at four rates of paraquat (15, 45, 135 and 270 g/ha paraquat ion). All treatments were made up in deionised water and applied using a
- 20 tracksprayer with a 11002 nozzle at a spray application volume of 200l/ha. All treatments were replicated 3 times. After spraying the plants were laid out in a glass-house and maintained at a temperature of 22°C by day and 18°C by night. A visual assessment of % control was carried out 18 days after treatment and calculated doses for 90% control (ED90 - g paraquat ion per litre) were calculated. The adjuvants were applied at 0.1% w/v.
- 25 ED90 g/ha 18DAT

Treatment (0.1% adjuvant)	ABUTH	SIDSP
Control - No adjuvant	325	(>270)
JEFFAMINE ED600	246	182

Claims

1. An agrochemical composition comprising an agrochemical active ingredient and an adjuvant of formula (I) and salts thereof



wherein R^1 and R^2 are independently hydrogen or a lower alkyl group or a group $X'-(R^3O)_a-R^4$ - wherein R^3 and R^4 respectively may take any of the values of R^3 and R^4 as hereinafter defined and wherein X' is -OH or a lower alkoxy group containing from 1 to 6 carbon atoms and a is from 0 to 400

R^3O is an ethoxy, propoxy or butoxy group or a random or block mixture thereof, R^4 is a linear or branched chain alkylene bridging group containing from 1 to 4 carbon atoms, X is

(IA) -OH or a lower alkoxy group containing from 1 to 6 carbon atoms or X is

(IB) a group R^5R^6N - or $R^5R^6N-R^7$ -

wherein R^5 and R^6 are independently hydrogen or a lower alkyl group or a group $X'-(R^3O)_a-R^4$ - as hereinbefore defined wherein X' is -OH or a lower alkoxy group containing from 1 to 6 carbon atoms,

and R^7 is a linear or branched chain alkylene bridging group containing from 1 to 4 carbon atoms

or X is

(IC) a group

$CR^{16}R^{17}-O-$

$|$
 $CR^{18}-(R^{21})_d-O-(R^8O)_b-R^9-NR^{10}R^{11}$

$|$
 $CR^{19}R^{20}-O-(R^{12}O)_c-R^{13}-NR^{14}R^{15}$

wherein R^{10} , R^{11} , R^{14} and R^{15} are independently hydrogen or a lower alkyl group or a group $X'-(R^3O)_a-R^4$ - as hereinbefore defined wherein X' is -OH or a lower alkoxy group containing from 1 to 6 carbon atoms,

and R^8 and R^{12} are independently alkyl groups containing from 1 to 4 carbon atoms and R^9 , R^{13} and R^{21} are independently a linear or branched chain alkylene bridging group containing from 1 to 6 carbon atoms, R^{16} , R^{17} , R^{18} , R^{19} and R^{20} are independently hydrogen or a lower alkyl group and d is 0 or 1
 5 and wherein a, is from 1 to 400 or if X is of formula IC, the sum of a, b and c is from 3 to 400.

2. A composition according to claim 1 wherein

X is -OH or a lower alkoxy group containing from 1 to 4 carbon atoms or

X is R^5R^6N - wherein R^5 and R^6 are hydrogen or a lower alkyl group containing from
 10 1 to 4 carbon atoms or

X is a group of formula IC'

$CH_2 - O -$

$|$
 $CR^{18} - (R^{21})_d - O - (R^8O)_b - R^9 - NH_2$

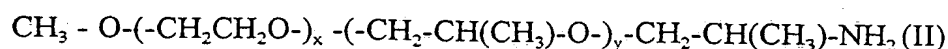
$|$
 $CH_2 - O - (R^{12}O)_c - R^{13} - NH_2$

wherein R^8O and $R^{12}O$ are independently ethoxy, or propoxy or a random or block mixture thereof, R^9 and R^{13} are independently a linear or branched chain alkylene bridging group containing 2 or 3 carbon atoms, R^{21} is a linear or branched chain
 20 alkylene bridging group containing from 1 to 3 carbon atoms, R^{18} is hydrogen or lower alkyl containing from 1 to 4 carbon atoms, d is 0 or 1,

R^1 and R^2 are independently hydrogen or a lower alkyl group containing from 1 to 4 carbon atoms, R^3O is ethoxy, or propoxy or a random or block mixture thereof, R^4 is a linear or branched chain alkylene bridging group containing 2 or 3 carbon atoms
 25 and a is from 1 to 400 or if X is of formula IC', the sum of a, b and c is from 3 to 400.

3. A composition according to claim 1 or 2 wherein a is from 1 to 50 or if X is of formula IC or IC' respectively, the sum of a, b and c is from 3 to 90 and wherein in the group $X' - (R^3O)_a - R^4$ - if present, a' is from 0 to 50.

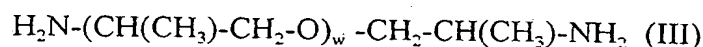
30 4. A composition according to claim 1 wherein the adjuvant of formula (I) is an alkoxyated monoamine, having the formula II



wherein the average degree of ethoxylation (x) is from 0 to about 45 and the average degree of propoxylation (y) is from 0 to about 90 provided that x and y are not both 0 at the same time.

5. A composition according to claim 4 wherein the value of x is from 0 to about 20 and of y is from about 2 to about 30.

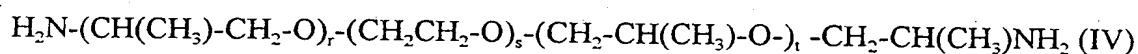
6. A composition according to claim 1 wherein the compound of formula (I) is a diamine having a formula (II)



wherein w is an average of from about 1 to about 80.

7. A composition according to claim 6 wherein w is an average of from about 2 to about 35

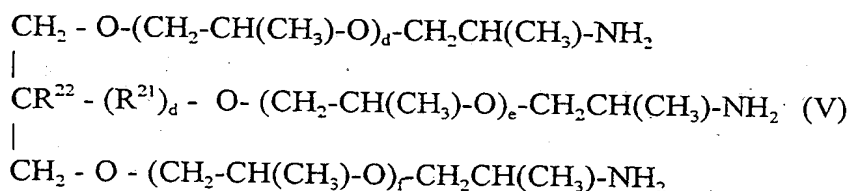
8. A composition according to claim 1 wherein the compound of formula (I) is a diamine having a formula (IV)



wherein the sum of r + t is an average of from 1 to 20 propoxy groups and s is an average of from 2 to 50 ethoxy units.

9. A composition according to claim 8 wherein the sum of r + t is from about 2 to about 15 and s is from about 3 to about 20.

10. A composition according to claim 1 wherein the compound of formula (I) is a propoxylated triamine having the formula (V)



wherein the sum of d + e + f is an average of from about 5 to 90, R²² is hydrogen or lower alkyl containing 1 to 4 carbon atoms, R²¹ is a linear or branched chain alkylene bridging group containing 1 to 3 carbon atoms and d is 0 or 1.

11. A composition according to any of the preceding claims wherein the proportion of adjuvant of formula (I) to the agrochemical is from 1:20 to 3:1 by weight.

12. A composition according to any of the preceding claims wherein the adjuvant of formula (I) in claim 1 is used in combination with an alkylpolyglycoside surfactant.

13. A composition according to claim 12 wherein the ratio of the adjuvant of formula (I) to the alkylpolyglycoside surfactant is from 1 : 40 to 4 : 1.
14. A composition according to any of the preceding claims wherein the agrochemical active ingredient is a salt of glyphosate, a salt of fomesafen or a paraquat salt.
- 5 15. A composition according to any of claims 1 to 13 wherein the adjuvant of formula (I) in claim 1 is used in the form of a salt with glyphosate or a salt with an acidic surfactant.
16. A process of severely damaging or killing unwanted plants which process comprises applying to the plants or to the growth medium of the plants, a herbicidally effective
10 amount of a composition as claimed in claim 14.
17. A composition according to any of claims 1 to 15 which is an aqueous composition containing from 0.01% to 90% by weight of the active ingredient.